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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. MI22-1385

First Inventor or Application Identifier Gurtej S. Sandhu

Title Deposition Methods and Apparatuses Providing Surface Activation

Express Mail Label No. EL465688196US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents
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1. ☒ * Fee Transmittal Form (e.g., PTO/SB/17)
 (Submit an original and a duplicate for fee processing)
2. ☒ Specification [Total Pages 39]
 (preferred arrangement set forth below)
 - Descriptive title of the Invention
 - Cross References to Related Applications
 - Statement Regarding Fed sponsored R & D
 - Reference to Microfiche Appendix
 - Background of the Invention
 - Brief Summary of the Invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
3. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 3]
 4. Oath or Declaration [Total Pages]
 a. ☐ Newly executed (original or copy)
 b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))
 (for continuation/divisional with Box 16 completed)
 i. ☐ DELETION OF INVENTOR(S)
 Signed statement attached deleting
 inventor(s) named in the prior application,
 see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission
 (if applicable, all necessary)
 a. ☐ Computer Readable Copy
 b. ☐ Paper Copy (identical to computer copy)
 c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

7. ☐ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R. § 3.73(b) Statement of Power of Attorney
 (when there is an assignee)
9. ☐ English Translation Document (if applicable)
10. ☐ Information Disclosure Statement (IDS)/PTO-1449 [Copies of IDS Citations]
11. ☐ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503)
 (Should be specifically itemized)
13. ☐ * Small Entity Statement(s) [Statement filed in prior application Status still proper and desired (PTO/SB/09-12)]
14. ☐ Certified Copy of Priority Document(s)
 (if foreign priority is claimed)
15. ☒ Other: Check in the amount of \$1536.00

* NOTE FOR ITEMS 1 & 13 IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No: _____
 Prior application information: Examiner _____ Group / Art Unit: _____

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James E. Lake

Registration No. (Attorney/Agent)

44,854

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TOTAL AMOUNT OF PAYMENT (\$1536.00)

Complete if Known

Application Number	Unknown
Filing Date	August 31, 2000
First Named Inventor	Gurtej S. Sandhu
Examiner Name	Unassigned
Group / Art Unit	Unassigned
Attorney Docket No.	MI22-1385

METHOD OF PAYMENT (check one)

1. ☒ The Commissioner is hereby authorized to charge indicated fees and credit any over payments to:

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23-0925

Wells, St. John

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2. ☒ Payment Enclosed:

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FEE CALCULATION

1. BASIC FILING FEE

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description	Fee Paid
101	760	201	380	Utility filing fee	690.00
106	310	206	155	Design filing fee	
107	480	207	240	Plant filing fee	
108	760	208	380	Reissue filing fee	
114	150	214	75	Provisional filing fee	

SUBTOTAL (1) (\$690.00)

2. EXTRA CLAIM FEES

Total Claims	Extra Claims	Fee from below	Fee Paid
54	-20** = 34	18.00	612.00
Independent Claims	6	-3** = 3	78.00
Multiple Dependent			0.00

**or number previously paid, if greater; For Reissues, see below

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description
103	18	203	9	Claims in excess of 20
102	78	202	39	Independent claims in excess of 3
104	260	204	130	Multiple dependent claim, if not paid
109	78	209	39	** Reissue independent claims over original patent
110	18	210	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) (\$846.00)

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	0.00
127	50	227	25	Surcharge - late provisional filing fee or cover sheet.	0.00
139	130	139	130	Non-English specification	0.00
147	2,520	147	2,520	For filing a request for reexamination	0.00
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	0.00
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	0.00
115	110	215	55	Extension for reply within first month	0.00
116	380	216	190	Extension for reply within second month	0.00
117	870	217	435	Extension for reply within third month	0.00
118	1,360	218	680	Extension for reply within fourth month	0.00
128	1,850	228	925	Extension for reply within fifth month	0.00
119	300	219	150	Notice of Appeal	0.00
120	300	220	150	Filing a brief in support of an appeal	0.00
121	260	221	130	Request for oral hearing	0.00
138	1,510	138	1,510	Petition to institute a public use proceeding	0.00
140	110	240	55	Petition to revive - unavoidable	0.00
141	1,210	241	605	Petition to revive - unintentional	0.00
142	1,210	242	605	Utility issue fee (or reissue)	0.00
143	430	243	215	Design issue fee	0.00
144	580	244	290	Plant issue fee	0.00
122	130	122	130	Petitions to the Commissioner	0.00
123	50	123	50	Petitions related to provisional applications	0.00
126	240	126	240	Submission of Information Disclosure Stmt	0.00
581	40	581	40	Recording each patent assignment per property (times number of properties)	0.00
146	760	246	380	Filing a submission after final rejection (37 CFR 1.129(a))	0.00
149	760	249	380	For each additional invention to be examined (37 CFR 1.129(b))	0.00
Other fee (specify) _____					0.00
Other fee (specify) _____					0.00

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SUBMITTED BY

Typed or
Printed Name James E. Lake

Signature

Date 31 Aug 00

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EL465688196US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR LETTERS PATENT

* * * * *

**DEPOSITION METHODS AND
APPARATUSES PROVIDING
SURFACE ACTIVATION**

* * * * *

INVENTORS

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ATTORNEY'S DOCKET NO. MI22-1385

1 **DEPOSITION METHODS AND APPARATUSES**
2 **PROVIDING SURFACE ACTIVATION**

3 **TECHNICAL FIELD**

4 This invention relates to deposition methods including surface
5 activation of a substrate and deposition apparatuses providing surface
6 activation of a substrate.

7
8 **BACKGROUND OF THE INVENTION**

9 Atomic layer deposition (ALD) is recognized as a deposition
10 technique that forms high quality materials with minimal defects and
11 tight statistical process control. Even so, it is equally recognized that
12 ALD can have limited application. In some circumstances, the
13 theoretically expected quality of an ALD layer is not achieved.

14 It can be seen that a need exists for an ALD method that forms
15 a layer without introducing intolerable defects into the material.

16
17 **SUMMARY OF THE INVENTION**

18 According to one aspect of the invention, a deposition method
19 includes, at a first temperature, contacting a substrate with a surface
20 activation agent and adsorbing a first layer over the substrate. At a
21 second temperature greater than the first temperature, the first layer may
22 be contacted with a first precursor and a second layer may be
23 chemisorbed at least one monolayer thick over the substrate. As an

1 example, the first layer may enhance a chemisorption rate of the first
2 precursor compared to the substrate without the surface activation agent
3 adsorbed thereon. Also, the first temperature may be less than a
4 chemisorption temperature of the surface activation agent on the
5 substrate. The first and second temperatures may be those of at least
6 a portion of the substrate, those of an outermost surface of the
7 substrate, or, respectively, those of the surface activation agent and first
8 precursor. The second layer may be chemisorbed on the first layer, or
9 the method may include substantially displacing the first layer from over
10 the substrate during chemisorption of the first layer on the substrate.

11 In another aspect of the invention, a deposition method includes,
12 at an initial temperature less than a chemisorption temperature of a
13 surface activation agent, adsorbing the agent over a substrate. At a
14 deposition temperature greater than the initial temperature, a first species
15 may be atomic layer deposited over the substrate. As an example, the
16 surface activation agent may enhance an atomic layer deposition rate of
17 the first species compared to the substrate without the surface activation
18 agent adsorbed thereon. The method may further include atomic layer
19 depositing a second species on the atomic layer deposited first species,
20 the deposited first and second species combined comprising a deposition
21 material.

22 In a further aspect of the invention, a deposition method includes
23 adsorbing a surface activation agent over a substrate, at least an outer

1 surface of the substrate being at a first temperature less than a
2 chemisorption temperature of the agent. A temperature of at least a
3 portion of the substrate may then be altered. A monolayer of a first
4 compound may be chemisorbed over the substrate, at least an outer
5 surface of the substrate being at a second temperature greater than the
6 first temperature. The agent may be substantially displaced from over
7 the substrate and a monolayer of a second compound may be
8 chemisorbed on the first compound monolayer.

9 A still further aspect of the invention includes a deposition method
10 of contacting a bulk semiconductor wafer with a cooling medium to
11 establish at least an outer surface of the wafer at an initial temperature.
12 The wafer may be contacted with a surface activation agent, adsorbing
13 a first layer on the wafer. The initial temperature may be less than a
14 chemisorption temperature of the agent. The wafer may be placed on
15 a heated wafer chuck, establishing at least an outer surface of the wafer
16 at a deposition temperature greater than the initial temperature. The
17 first layer may be contacted with a deposition precursor, chemisorbing a
18 second layer at least one monolayer thick over the wafer. Examples of
19 contacting with a cooling medium include elevating the wafer over the
20 heated wafer chuck and contacting the wafer with cooling gases as well
21 as placing the wafer on a cooled wafer chuck different from the heated
22 wafer chuck.

1 Other aspects of the invention include deposition apparatuses. One
2 such apparatus includes a deposition chamber having at least one
3 precursor gas dispenser in each of at least one contacting zone and at
4 least one cooling gas dispenser in each of at least one cooling zone.
5 A substrate chuck moves by linear translational motion from the at least
6 one contacting zone to the at least one cooling zone. The substrate
7 chuck includes a substrate lift that positions a deposition substrate at an
8 elevation above the heated surface of the substrate chuck when
9 dispensing a cooling gas in the at least one cooling zone and when
10 dispensing a surface activation agent in the at least one contacting zone.
11 An exemplary deposition chamber has two contacting zones and one
12 cooling zone. The substrate chuck moves from one contacting zone
13 through the cooling zone to another contacting zone. Contacting and
14 cooling zones may be established with at least one of an inert gas
15 curtain or suitable gas flow conditions. Also, the substrate lift may
16 comprise positioning pins of a substrate chuck.

17 Another deposition apparatus includes at least one cooling chamber
18 having a cooled substrate chuck and at least one contacting chamber
19 having a heated substrate chuck. The contacting chamber may also have
20 at least one precursor gas dispenser. The heated substrate chuck may
21 include a substrate lift that positions a deposition substrate at an
22 elevation above a heated surface of the heated substrate chuck when
23 dispensing a surface activation agent in the contacting chamber. A

1 robotic substrate handler may move a substrate from the at least one
2 cooled substrate chuck to the at least one heated substrate chuck.

3 4 **BRIEF DESCRIPTION OF THE DRAWINGS**

5 Preferred embodiments of the invention are described below with
6 reference to the following accompanying drawings.

7 Figs. 1-4 are line charts respectively showing the timing for
8 contacting a substrate in an atomic layer deposition process with a
9 surface activation agent, precursor 1, precursor 2, and purge gas.

10 Fig. 5 is a line chart showing the timing for altering temperature
11 during the contacting described in Figs. 1-4.

12 Fig. 6 shows a diagrammatic view of a deposition apparatus
13 according to one aspect of the invention at a processing step according
14 to another aspect of the present invention.

15 Fig. 7 shows the deposition apparatus of Fig. 6 at a processing
16 step subsequent to that shown in Fig. 6.

17 Fig. 8 shows a diagrammatic view of an alternative deposition
18 apparatus according to a further aspect of the invention at a processing
19 step according to yet another aspect of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

Atomic layer deposition (ALD) involves formation of successive atomic layers on a substrate. Such layers may comprise an epitaxial, polycrystalline, amorphous, etc. material. ALD may also be referred to as atomic layer epitaxy, atomic layer processing, etc. Further, the invention may encompass other deposition methods not traditionally referred to as ALD, for example, chemical vapor deposition (CVD), but nevertheless including the method steps described herein. The deposition methods herein may be described in the context of formation on a semiconductor wafer. However, the invention encompasses deposition on a variety of substrates besides semiconductor substrates.

In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above.

Described in summary, ALD includes exposing an initial substrate to a first chemical species to accomplish chemisorption of the species onto the substrate. Theoretically, the chemisorption forms a monolayer that is uniformly one atom or molecule thick on the entire exposed initial substrate. In other words, a saturated monolayer. Practically, as further described below, chemisorption might not occur on all portions of the substrate. Nevertheless, such an imperfect monolayer is still a monolayer in the context of this document. In many applications, merely a substantially saturated monolayer may be suitable. A substantially saturated monolayer is one that will still yield a deposited layer exhibiting the quality and/or properties desired for such layer.

The first species is purged from over the substrate and a second chemical species is provided to chemisorb onto the first monolayer of the first species. The second species is then purged and the steps are repeated with exposure of the second species monolayer to the first species. In some cases, the two monolayers may be of the same species. Also, a third species or more may be successively chemisorbed and purged just as described for the first and second species.

Purging may involve a variety of techniques including, but not limited to, contacting the substrate and/or monolayer with a carrier gas and/or lowering pressure to below the deposition pressure to reduce the concentration of a species contacting the substrate and/or chemisorbed species. Examples of carrier gases include N₂, Ar, He, Ne, Kr, Xe, etc.

1 Purging may instead include contacting the substrate and/or monolayer
2 with any substance that allows chemisorption byproducts to desorb and
3 reduces the concentration of a contacting species preparatory to
4 introducing another species. A suitable amount of purging can be
5 determined experimentally as known to those skilled in the art. Purging
6 time may be successively reduced to a purge time that yields an increase
7 in film growth rate. The increase in film growth rate might be an
8 indication of a change to a non-ALD process regime and may be used
9 to establish a purge time limit.

10 ALD is often described as a self-limiting process, in that a finite
11 number of sites exist on a substrate to which the first species may form
12 chemical bonds. The second species might only bond to the first species
13 and thus may also be self-limiting. Once all of the finite number of
14 sites on a substrate are bonded with a first species, the first species will
15 often not bond to other of the first species already bonded with the
16 substrate. However, process conditions can be varied in ALD to
17 promote such bonding and render ALD not self-limiting. Accordingly,
18 ALD may also encompass a species forming other than one monolayer
19 at a time by stacking of a species, forming a layer more than one atom
20 or molecule thick. The various aspects of the present invention
21 described herein are applicable to any circumstance where ALD may be
22 desired. A few examples of materials that may be deposited by ALD
23

1 include silicon nitride, zirconium oxide, tantalum oxide, aluminum oxide,
2 and others.

3 Often, traditional ALD occurs within an often-used range of
4 temperature and pressure and according to established purging criteria
5 to achieve the desired formation of an overall ALD layer one monolayer
6 at a time. Even so, ALD conditions can vary greatly depending on the
7 particular precursors, layer composition, deposition equipment, and other
8 factors according to criteria known by those skilled in the art.
9 Maintaining the traditional conditions of temperature, pressure, and
10 purging minimizes unwanted reactions that may impact monolayer
11 formation and quality of the resulting overall ALD layer. Accordingly,
12 operating outside the traditional temperature and pressure ranges may
13 risk formation of defective monolayers.

14 The general technology of chemical vapor deposition (CVD)
15 includes a variety of more specific processes, including, but not limited
16 to, plasma enhanced CVD and others. CVD is commonly used to form
17 non-selectively a complete, deposited material on a substrate. One
18 characteristic of CVD is the simultaneous presence of multiple species
19 in the deposition chamber that react to form the deposited material.
20 Such condition is contrasted with the purging criteria for traditional ALD
21 wherein a substrate is contacted with a single deposition species that
22 chemisorbs to a substrate or previously deposited species. An ALD
23 process regime may provide a simultaneously contacted plurality of

1 species of a type or under conditions such that ALD chemisorption,
2 rather than CVD reaction occurs. Instead of reacting together, the
3 species may chemisorb to a substrate or previously deposited species,
4 providing a surface onto which subsequent species may next chemisorb
5 to form a complete layer of desired material.

6 Under most CVD conditions, deposition occurs largely independent
7 of the composition or surface properties of an underlying substrate. By
8 contrast, chemisorption rate in ALD might be influenced by the
9 composition, crystalline structure, and other properties of a substrate or
10 chemisorbed species. Other process conditions, for example, pressure and
11 temperature, may also influence chemisorption rate. Accordingly,
12 observation indicates that chemisorption might not occur appreciably on
13 portions of a substrate though it occurs at a suitable rate on other
14 portions of the same substrate. Such a condition may introduce
15 intolerable defects into a deposited material.

16 According to one aspect of the invention, a deposition method may
17 include, at a first temperature, contacting a substrate with a surface
18 activation agent and adsorbing a first layer over the substrate. At a
19 second temperature greater than the first temperature, the first layer may
20 be contacted with a first precursor. A second layer may be chemisorbed
21 at least one monolayer thick over the substrate. Advantageously, the
22 first layer may enhance a chemisorption rate of the first precursor
23 compared to the substrate without the surface activation agent adsorbed

1 thereon. Enhancement of a chemisorption rate of the first precursor
2 may occur in a variety of ways. For example, where chemisorption of
3 the first precursor does not occur uniformly across the substrate, the
4 surface activation agent may provide chemisorption at substantially the
5 same rate, but uniformly across the substrate. Also, a surface activation
6 agent may increase chemisorption rate over regions of a substrate where
7 chemisorption normally would occur, but at a slower rate. The observed
8 effect of either enhancement will be to increase the average
9 chemisorption rate over all of the substrate.

10 Within the context of this document, "adsorption" refers to surface
11 retention of solid, liquid, or gas molecules, atoms, or ions by a solid or
12 liquid, as opposed to "absorption," the penetration of substances into the
13 bulk of the solid or liquid. Further, in the context of this document,
14 chemisorption refers to a type of adsorption in which chemical bonds are
15 formed between solid, liquid, or gas molecules, atoms, or ions and a
16 solid or liquid surface. The chemical bonds may be weak chemical
17 bonds.

18 It is a disadvantage of some deposition methods, for example ALD,
19 that nonuniform deposition may occur over regions of a substrate where
20 some difference in surface properties or composition exists in the
21 substrate. By adsorbing a first layer including a surface activation agent
22 over a substrate at a first temperature less than a chemisorption
23 temperature of the surface activation agent on the substrate, more

1 uniform formation of the first layer may be established. The second
2 layer including the first precursor may be chemisorbed on the first layer.
3 Alternatively, the method may include substantially displacing the first
4 layer from over the substrate during the chemisorbing second layer. In
5 such a circumstance, the second layer may be chemisorbed on the
6 substrate. In substantially displacing the surface activation agent, a
7 negligible amount of surface activation agent may remain on which the
8 first precursor may or may not chemisorb. However, substantially
9 displacing the surface activation agent is sufficient to establish a
10 deposited material having the desired properties. Adsorbing the first
11 layer, but not chemisorbing the first layer, may provide a more uniform
12 layer of a surface activation agent than would be established in
13 chemisorption of the same agent or material.

14 A variety of surface activation means may be utilized, for example,
15 the surface activation agent may be the same as the first precursor or
16 the surface activation agent may be different from any other precursors
17 used in a deposition method. For example, and preferably, the surface
18 activation agent may be a metal halide, a metal organic, an alcohol, a
19 carboxylic acid, or an amine. Also for example, and more preferably,
20 the surface activation agent may be at least one of TiCl_4 , WF_6 ,
21 hexamethyldisilazane, tetrakis(dimethylamido)titanium,
22 tetraethylorthosilicate, H_2O , methanol, ethanol, isopropanol, formic acid,
23 acetic acid, oxalic acid, NH_3 , methylamine, ethylamine, or dimethylamine.

1 Contacting of the substrate may comprise contacting a bulk
2 semiconductor wafer, or some other material formed over such a wafer,
3 wherein such contacting initiates formation of a new material.
4 Alternatively, contacting a substrate may include contacting a previously
5 chemisorbed layer of a deposition precursor and adsorbing the surface
6 activation agent on the previously chemisorbed layer. That is, adsorbing
7 a surface activation agent may be advantageous both in initiating a
8 deposition method as well as continuing a deposition method after
9 initiation.

10 A variety of processing conditions may also be suitable according
11 to various aspects of the invention. For example, at a first temperature,
12 when contacting a substrate with a surface activation agent and, at a
13 second temperature, contacting the surface activation agent with a first
14 precursor, the first and second temperatures may be those of at least a
15 portion of the substrate. Also, the first and second temperatures may
16 be those of an outermost surface of the substrate. Still further, the first
17 and second temperatures may be, respectively, those of the surface
18 activation agent and the first precursor. Actual first and second
19 temperatures will depend largely on the individual properties of the
20 surface activation agent and the first precursor as well as a desired
21 deposition material.

22 Also, chemisorbing the second layer may be accomplished in a
23 variety of ways. The first precursor may consist essentially of a single

precursor species. Alternatively, as discussed above, a plurality of species may be used as the first precursor. The second layer chemisorbed from the first precursor may consist essentially of a monolayer. Further, the method may include contacting the second layer with a second precursor and chemisorbing at least one monolayer thick on the second layer. A chemisorption product of the first and second precursors may form a deposition material. The chemisorption product may consist essentially of a monolayer of the deposition material.

As another aspect of the invention, a deposition method may include, at an initial temperature less than a chemisorption temperature of a surface activation agent, adsorbing the agent over a substrate. At a deposition temperature greater than the initial temperature, a first species may be atomic layer deposited over the substrate. Similar surface activation agents to those described above may be used. Such a surface activation agent may enhance an atomic layer deposition rate of the first species compared to the substrate without the surface activation agent adsorbed thereon. The initial and deposition temperatures may be those of at least a portion of the substrate, as well as other substances, such as those described above. The method may further include atomic layer depositing a second species on the atomic layer deposited first species. The deposited first and second species combined may comprise a deposition material.

1 As a further aspect of the invention, a deposition method may
2 include adsorbing a surface activation agent over a substrate. At least
3 an outer surface of the substrate may be at a first temperature less than
4 a chemisorption temperature of the agent. A temperature of at least a
5 portion of the substrate may then be altered and a monolayer of a first
6 compound may be chemisorbed over the substrate. At least an outer
7 surface of the substrate may be at a second temperature greater than
8 the first temperature. The chemisorption may substantially displace the
9 agent from over the substrate. The method may further include
10 chemisorbing a monolayer of a second compound on the first compound
11 monolayer. As before, the adsorbed surface activation agent may
12 advantageously enhance a chemisorption rate of the first compound
13 compared to the substrate without the surface activation agent adsorbed
14 thereon.

15 A still further aspect of the invention provides a deposition method
16 that includes contacting a bulk semiconductor wafer with a cooling
17 medium to establish at least an outer surface of the wafer at an initial
18 temperature. The wafer may be contacted with a surface activation
19 agent, adsorbing a first layer on the wafer. The initial temperature may
20 be less than a chemisorption temperature of the agent. The wafer may
21 be placed on a heated wafer chuck and at least an outer surface of the
22 wafer established at a deposition temperature greater than the initial
23 temperature. The first layer may be contacted with a deposition

precursor, chemisorbing a second layer at least one monolayer thick over the wafer. In keeping with the previous description, the first layer may enhance a chemisorption rate of the deposition precursor compared to the wafer without the surface activation agent adsorbed thereon. Also, the surface activation agent may be the same as the deposition precursor or, alternatively, different.

Contacting with the cooling medium may be accomplished in a variety of ways. As one example, the wafer may be elevated over the heated wafer chuck and contacted with cooling gases. Placing the wafer on the heated wafer chuck may include lowering the wafer from the position where the wafer was contacted with cooling gases. Also, for example, contacting the wafer with a cooling medium may include placing the wafer on a cooled wafer chuck different from the heated wafer chuck.

Contacting the wafer with a surface activation agent and deposition precursor may also be accomplished in a variety of ways. For example, the wafer may be moved within a single chamber of a deposition apparatus from a first zone containing a surface activation agent to a second zone containing the deposition precursor. The moving may be accomplished by linear translational motion of the heated wafer chuck. Also for example, the wafer may be moved from a cooled wafer chuck in a first chamber of a multiple chamber deposition apparatus to a second chamber of the apparatus wherein contacting with the agent and

1 contacting with the precursor may occur. The moving may be
2 accomplished by a robotic wafer handler.

3 Accordingly, other aspects of the invention include deposition
4 apparatuses that accomplish surface activation of a substrate. One
5 exemplary deposition apparatus includes a deposition chamber having at
6 least one precursor gas dispenser in each of at least one contacting zone
7 and at least one cooling gas dispenser in each of at least one cooling
8 zone. A substrate chuck moves by linear translational motion from the
9 at least one contacting zone to the at least one cooling zone. The
10 substrate chuck may include a substrate lift that positions a deposition
11 substrate at an elevation above a heated surface of the substrate chuck.
12 Such positioning of a deposition substrate may occur when dispensing a
13 cooling gas in the at least one cooling zone and when dispensing a
14 surface activation agent in the at least one contacting zone.

15 Figs. 6 and 7 show a deposition apparatus 2 with a deposition
16 chamber 4 having a contacting zone 20 and a contacting zone 24 as well
17 as a cooling zone 22. Precursor gas dispenser 6 supplies gases 6a
18 and/or 6b to contacting zone 20. Precursor gas dispenser 10 supplies
19 gases 10a and/or 10b to contacting zone 24. Cooling gas dispenser 8
20 supplies gas 8a to cooling zone 22. Zone boundaries 18 isolate
21 contacting zone 20 from cooling zone 22 and contacting zone 24 from
22 cooling zone 22.

1 Isolation of zones 20, 22, and 24 within deposition chamber 4 may
2 be accomplished in a variety of ways. As one example, contacting and
3 cooling zones may be established with an inert gas curtain as known to
4 those skilled in the art. Nitrogen, Ar, and He are examples of suitable
5 inert gases. Also, such zones may be established using suitable gas flow
6 conditions as known to those skilled in the art. For example, laminar
7 flow conditions may be suitable. The suitability of particular conditions
8 may be experimentally determined in any manner known to those skilled
9 in the art for a particular deposition chamber and combination of gases
10 and apparatuses inside the chamber that can affect gas mixing. The gas
11 flow conditions may minimize mixing of flowing gases in contacting and
12 cooling zones such that only negligible mixing occurs of supplied gases
13 in a region defined as a zone boundary, for example, zone boundaries
14 18. Further, the cooling zone may consist essentially of an inert gas
15 curtain isolating two contacting zones. For example, gas 8a may be a
16 cooling gas as well as an inert gas such that no separate inert gas
17 curtain is desired to isolate contacting zone 20 from cooling zone 22 and
18 contacting zone 24 from cooling zone 22.

19 Fig. 6 also shows a wafer chuck 12 having positioning pins 14 as
20 a substrate lift upon which wafer 16 is placed. Positioning pins 14
21 position wafer 16 at an elevation above wafer chuck 12. Accordingly,
22 when wafer chuck 12 is heated, wafer 16 will be distanced from a
23

1 heated surface of wafer chuck 12 for cooling of at least an outer surface
2 of wafer 16 by gas 8a.

3 As shown in Fig. 7, wafer chuck 12 may move by linear
4 translational motion from cooling zone 22 to contacting zone 20 and
5 positioning pins 14 may lower wafer 16 from the elevation above the
6 heated surface of wafer chuck 12. Fig. 7 shows wafer 16 completely
7 lowered so as to rest on wafer chuck 12, however, an intermediate
8 position between the positions shown in Figs. 6 and 7 may also be
9 suitable. Gases 6a and/or 6b may be dispensed from precursor gas
10 dispenser 6 with wafer 16 in a lowered position to accomplish
11 chemisorption of a deposition precursor on wafer 16. Although not
12 shown, wafer chuck 12 may also move into contacting zone 24 without
13 lowering positioning pins 14 to accomplish adsorption of a surface
14 activation agent dispensed from precursor gas dispenser 10 at the
15 temperature established in cooling zone 22. Accordingly, substrate chuck
16 12 may move from one contacting zone through cooling zone 22 to
17 another contacting zone in performing a deposition method such as the
18 various methods described herein. Temperature, contacting of surface
19 activation agents and precursors, chemisorption, and adsorption may be
20 controlled as preferred accordingly to the various aspects of the invention
21 using the apparatus of Figs. 6 and 7.

22 Similarly, such methods may also be practiced in a deposition
23 apparatus that includes at least one cooling chamber having a cooled

1 substrate chuck and at least one contacting chamber having at least one
2 precursor gas dispenser. The at least one contacting chamber may also
3 have a heated substrate chuck including a substrate lift that positions a
4 deposition substrate at an elevation above a heated surface of the heated
5 substrate chuck when dispensing a surface activation agent in the
6 contacting chamber. A robotic substrate handler may be provided that
7 moves a substrate from the at least one cooled substrate chuck to the
8 at least one heated substrate chuck. One example of such an apparatus
9 is shown in Fig. 8.

10 Deposition apparatus 30 of Fig. 8 includes a contacting chamber
11 40 and a cooling chamber 42. A heated wafer chuck 32 provided in
12 contacting chamber 40 includes positioning pins 34 analogous to
13 positioning pins 14 shown in Figs. 6 and 7. Positioning pins 34 are
14 shown in Fig. 8 in a raised position. A gas dispenser 38 supplies gases
15 38a and/or 38b to contacting chamber 40. Cooling chamber 42 includes
16 a cooled wafer chuck 36. Although not shown, a robotic wafer handler
17 moves wafer 16 from cooled wafer chuck 36 to heated wafer chuck 32.

18 When adsorbing a surface activation agent on wafer 16, positioning
19 pins 34 may operate as a substrate lift to elevate wafer 16 above the
20 heated surface of the substrate chuck. Accordingly, adsorption at a
21 temperature lower than that of heated wafer chuck 32 may be
22 accomplished. Positioning pins 34 may then lower wafer 16 from the
23 elevation above the heated surface to increase temperature and

1 accomplish chemisorption of a deposition precursor in contacting chamber
2 40. Accordingly, both a surface activation agent and a deposition
3 precursor may be supplied from gas dispenser 38 at appropriate times to
4 accomplish adsorption and chemisorption.

5 Turning to Figs. 1-5, a process regime is described for ALD that
6 is within the scope of the present invention. Figs. 1-4 show the cyclic
7 contacting and purging of a substrate with surface activation agent
8 (SAA), Precursor 1 (P1), and Precursor 2 (P2). As shown in Fig. 1, a
9 substrate is first contacted with SAA from Time 0 (T0) to Time 1 (T1).
10 An optional purge of SAA that is not adsorbed to a substrate may then
11 occur from T1 to T2. Such purge is optional depending on the
12 particular SAA and P1 selected. For example, if SAA and P1 are
13 identical, then it is conceivable that purging might not occur prior to
14 chemisorption of P1. Adsorbed SAA is then contacted with P1 from T2
15 to T3, chemisorbing P1 over the substrate. As discussed above, P1 may
16 chemisorb either to adsorbed SAA, to the substrate after displacing SAA,
17 or both. After purging excess P1 from T3 to T4, chemisorbed P1 is
18 contacted with P2 from T4 to T5. After purging excess P2 from T5 to
19 T6, the cycle begins again. However, the cycle may begin by either
20 contacting chemisorbed P2 with SAA or P1 from T6 to T7. As also
21 discussed above, it may be desirable only to adsorb SAA as an initial
22 layer or to adsorb SAA at the beginning of more than one cycle of
23 chemisorbing deposition precursors. Accordingly, contacting SAA from

1 T6 to T7 is shown in dashed outline as an optional step and contacting
2 with P1 from T6 to T7 is shown in dash-dot outline also indicating an
3 optional step.

4 The cycle from T0 to T5 thus may form at least a monolayer of
5 a chemisorption product of P1 and P2. The purge from T5 to T6
6 prepares the chemisorption product of P1 and P2 to begin a new cycle
7 at T6. Notably, the time intervals from T0 to T1 to T2, etc., are shown
8 as equal merely for graphical convenience. In practice, such times may
9 be individually determined according to the knowledge of those skilled
10 in the art considering the aspects and advantages of the inventions
11 described herein.

12 Fig. 5 shows altering the temperature, preferably substrate
13 temperature, as part of the described method. Temperature 1 (Temp1)
14 is maintained from T0 to T1 during contacting of SAA. Thereafter,
15 temperature is increased to Temp2 during purging from T1 to T2 and
16 maintained at Temp2 during contacting of P1, purging, and contacting of
17 P2 from T2 to T5. Depending on whether SAA or P1 will be contacted
18 from T6 to T7, temperature may be reduced from Temp2 to Temp1
19 from T5 to T6 or may remain at Temp2. Accordingly, temperature
20 remaining at Temp2 from T5 to T7 is shown in dash-dot outline to
21 correspond with contacting P1 and decreasing temperature is shown in
22 dashed outline to correspond with contacting SAA.

1 In keeping with the various aspects of the invention, other
2 scenarios of contacting surface activating agents and precursors and
3 altering temperatures are also conceivable, some of which are expressly
4 described herein. For example, since temperature changes are involved,
5 it is conceivable that a desired temperature might not be established
6 before starting contacting of a surface activation agent or precursor.
7 Rather, it may be suitable to establish such temperature some time after
8 the start of contacting. Consideration may be made regarding whether
9 the delay in establishing a temperature is justified by an improvement
10 in adsorption or chemisorption efficiency. That is, if a desired
11 temperature for chemisorption is established before contacting, then a
12 difference in chemisorption efficiency might exist compared to not
13 establishing the temperature until after contacting begins. Accordingly,
14 a deposition method according to the various aspects of the invention
15 herein may be optimized for processing time and efficiency depending on
16 the priorities and objectives of a particular process.

17 In compliance with the statute, the invention has been described
18 in language more or less specific as to structural and methodical
19 features. It is to be understood, however, that the invention is not
20 limited to the specific features shown and described, since the means
21 herein disclosed comprise preferred forms of putting the invention into
22 effect. The invention is, therefore, claimed in any of its forms or
23

1 modifications within the proper scope of the appended claims
2 appropriately interpreted in accordance with the doctrine of equivalents.
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CLAIMS:

1. A deposition method comprising:

at a first temperature, contacting a substrate with a surface activation agent and adsorbing a first layer over the substrate; and

at a second temperature greater than the first temperature, contacting the first layer with a first precursor and chemisorbing a second layer at least one monolayer thick over the substrate.

2. The deposition method of claim 1 wherein the first layer enhances a chemisorption rate of the first precursor compared to the substrate without the surface activation agent adsorbed thereon.

3. The deposition method of claim 1 wherein the surface activation agent comprises a metal halide, metal organic, alcohol, carboxylic acid, or amine.

4. The deposition method of claim 1 wherein the surface activation agent comprises at least one of TiCl_4 , WF_6 , hexamethyldisilazane, tetrakis(dimethylamido)titanium, tetraethylorthosilicate, H_2O , methanol, ethanol, isopropanol, formic acid, acetic acid, oxalic acid, NH_3 , methylamine, ethylamine, or dimethylamine.

1 5. The deposition method of claim 1 wherein the first
2 temperature is less than a chemisorption temperature of the surface
3 activation agent on the substrate.

4
5 6. The deposition method of claim 1 wherein the first and
6 second temperatures are those of at least a portion of the substrate.

7
8 7. The deposition method of claim 1 wherein the first and
9 second temperatures are those of an outermost surface of the substrate.

10
11 8. The deposition method of claim 1 wherein the first and
12 second temperatures are respectively those of the surface activation agent
13 and first precursor.

14
15 9. The deposition method of claim 1 wherein the substrate
16 comprises a bulk semiconductor wafer.

17
18 10. The deposition method of claim 1 wherein the second layer
19 is chemisorbed on the first layer.

1 11. The deposition method of claim 1 wherein the contacting the
2 substrate comprises contacting a previously chemisorbed layer of a
3 deposition precursor and adsorbing the surface activation agent on the
4 previously chemisorbed layer.

5
6 12. The deposition method of claim 1 further comprising
7 substantially displacing the first layer from over the substrate during the
8 chemisorbing the second layer.

9
10 13. The deposition method of claim 1 wherein the surface
11 activation agent is the same as the first precursor.

12
13 14. The deposition method of claim 1 wherein the second layer
14 consists essentially of a monolayer.

15
16 15. The deposition method of claim 1 wherein the first precursor
17 consists essentially of a single precursor species.

1 16. The deposition method of claim 1 further comprising
2 contacting the second layer with a second precursor and chemisorbing a
3 third layer at least one monolayer thick on the second layer, forming a
4 chemisorption product of the first and second precursors comprising a
5 deposition material.
6

7 17. The deposition method of claim 16 wherein the chemisorption
8 product consists essentially of a monolayer of the deposition material.
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1 18. A deposition method comprising:
2 at an initial temperature less than a chemisorption temperature of
3 a surface activation agent, adsorbing the agent over a substrate; and
4 at a deposition temperature greater than the initial temperature,
5 atomic layer depositing a first species over the substrate.

6
7 19. The deposition method of claim 18 wherein the surface
8 activation agent enhances an atomic layer deposition rate of the first
9 species compared to the substrate without the surface activation agent
10 adsorbed thereon.

11
12 20. The deposition method of claim 18 wherein the surface
13 activation agent comprises a metal halide, metal organic, alcohol,
14 carboxylic acid, or amine.

15
16 21. The deposition method of claim 18 wherein the surface
17 activation agent comprises at least one of TiCl_4 , WF_6 ,
18 hexamethyldisilazane, tetrakis(dimethylamido)titanium,
19 tetraethylorthosilicate, H_2O , methanol, ethanol, isopropanol, formic acid,
20 acetic acid, oxalic acid, NH_3 , methylamine, ethylamine, or dimethylamine.

1 22. The deposition method of claim 18 wherein the surface
2 activation agent is the same as the first species.

3
4 23. The deposition method of claim 18 wherein the initial and
5 deposition temperatures are those of at least a portion of the substrate.

6
7 24. The deposition method of claim 18 further comprising
8 substantially displacing the surface activation agent from over the
9 substrate during the atomic layer depositing the first species.

10
11 25. The deposition method of claim 18 further comprising atomic
12 layer depositing a second species on the atomic layer deposited first
13 species, the deposited first and second species combined comprising a
14 deposition material.

1 26. A deposition method comprising:

2 adsorbing a surface activation agent over a substrate, at least an
3 outer surface of the substrate being at a first temperature less than a
4 chemisorption temperature of the agent;

5 altering a temperature of at least a portion of the substrate;

6 chemisorbing a monolayer of a first compound over the substrate,
7 at least an outer surface of the substrate being at a second temperature
8 greater than the first temperature, and substantially displacing the agent
9 from over the substrate; and

10 chemisorbing a monolayer of a second compound on the first
11 compound monolayer.

12
13 27. The deposition method of claim 26 wherein the adsorbed
14 surface activation agent enhances a chemisorption rate of the first
15 compound compared to the substrate without the surface activation agent
16 adsorbed thereon.

17
18 28. The deposition method of claim 26 wherein the surface
19 activation agent comprises a metal halide, metal organic, alcohol,
20 carboxylic acid, or amine.

1 29. The deposition method of claim 26 wherein the surface
2 activation agent comprises at least one of TiCl_4 , WF_6 ,
3 hexamethyldisilazane, tetrakis(dimethylamido)titanium,
4 tetraethylorthosilicate, H_2O , methanol, ethanol, isopropanol, formic acid,
5 acetic acid, oxalic acid, NH_3 , methylamine, ethylamine, or dimethylamine.
6

7 30. The deposition method of claim 26 wherein the surface
8 activation agent is the same as the first compound.
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1 31. A deposition method comprising:

2 contacting a bulk semiconductor wafer with a cooling medium to
3 establish at least an outer surface of the wafer at an initial temperature;

4 contacting the wafer with a surface activation agent and adsorbing
5 a first layer on the wafer, the initial temperature being less than a
6 chemisorption temperature of the agent;

7 placing the wafer on a heated wafer chuck and establishing at least
8 the outer surface of the wafer at a deposition temperature greater than
9 the initial temperature; and

10 contacting the first layer with a deposition precursor and
11 chemisorbing a second layer at least one monolayer thick over the wafer.

12
13 32. The deposition method of claim 31 wherein the contacting
14 with the cooling medium comprises elevating the wafer over the heated
15 wafer chuck and contacting the wafer with cooling gases and wherein the
16 placing the wafer comprises lowering the wafer onto the heated wafer
17 chuck.

18
19 33. The deposition method of claim 31 wherein the contacting
20 with the cooling medium comprises placing the wafer on a cooled wafer
21 chuck different from the heated wafer chuck.

1 34. The deposition method of claim 31 wherein the contacting
2 with the surface activation agent and deposition precursor comprises
3 moving the wafer within a single chamber of a deposition apparatus from
4 a first zone containing the surface activation agent to a second zone
5 containing the deposition precursor.
6

7 35. The deposition method of claim 34 wherein the moving is
8 accomplished by linear translational motion of the heated wafer chuck.
9

10 36. The deposition method of claim 31 wherein the contacting
11 with the surface activation agent and deposition precursor comprises
12 moving the wafer from a cooled wafer chuck in a first chamber of a
13 multiple chamber deposition apparatus to a second chamber of the
14 apparatus wherein contacting with the agent and contacting with the
15 precursor may occur.
16

17 37. The deposition method of claim 36 wherein the moving is
18 accomplished by a robotic wafer handler.
19

20 38. The deposition method of claim 31 wherein the first layer
21 enhances a chemisorption rate of the deposition precursor compared to
22 the wafer without the surface activation agent adsorbed thereon.
23

1 39. The deposition method of claim 31 wherein the surface
2 activation agent comprises a metal halide, metal organic, alcohol,
3 carboxylic acid, or amine.
4

5 40. The deposition method of claim 31 wherein the surface
6 activation agent comprises at least one of TiCl_4 , WF_6 ,
7 hexamethyldisilazane, tetrakis(dimethylamido)titanium,
8 tetraethylorthosilicate, H_2O , methanol, ethanol, isopropanol, formic acid,
9 acetic acid, oxalic acid, NH_3 , methylamine, ethylamine, or dimethylamine.
10

11 41. The deposition method of claim 31 wherein the surface
12 activation agent is the same as the deposition precursor.
13

14 42. The deposition method of claim 31 wherein the second layer
15 consists essentially of a monolayer.
16

17 43. The deposition method of claim 31 wherein the deposition
18 precursor consists essentially of a single precursor species.
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1 44. A deposition apparatus comprising:

2 a deposition chamber having at least one precursor gas dispenser
3 in each of at least one contacting zone and at least one cooling gas
4 dispenser in each of at least one cooling zone; and

5 a substrate chuck that moves by linear translational motion from
6 the at least one contacting zone to the at least one cooling zone, the
7 substrate chuck comprising a substrate lift that positions a deposition
8 substrate at an elevation above a heated surface of the substrate chuck
9 when dispensing a cooling gas in the at least one cooling zone and when
10 dispensing a surface activation agent in the at least one contacting zone.

11
12 45. The apparatus of claim 44 wherein the substrate comprises
13 a bulk semiconductor wafer.

14
15 46. The apparatus of claim 44 wherein the deposition chamber
16 has two contacting zones and one cooling zone and the substrate chuck
17 moves from one contacting zone through the cooling zone to another
18 contacting zone.

19
20 47. The apparatus of claim 46 wherein the cooling zone consists
21 essentially of an inert gas curtain isolating the two contacting zones.

1 48. The apparatus of claim 44 wherein the substrate lift lowers
2 a deposition substrate from the elevation above the heated surface of the
3 substrate chuck when dispensing precursor gas in the at least one
4 contacting zone.

5
6 49. The apparatus of claim 44 wherein substrate lift comprises
7 positioning pins of the substrate chuck.

8
9 50. The apparatus of claim 44 wherein contacting and cooling
10 zones are established with at least one of an inert gas curtain or
11 suitable gas flow conditions.

1 51. A deposition apparatus comprising:

2 at least one cooling chamber having a cooled substrate chuck;

3 at least one contacting chamber having at least one precursor gas
4 dispenser and having a heated substrate chuck including a substrate lift
5 that positions a deposition substrate at an elevation above a heated
6 surface of the heated substrate chuck when dispensing a surface
7 activation agent in the contacting chamber; and

8 a robotic substrate handler that moves a substrate from the at
9 least one cooled substrate chuck to the at least one heated substrate
10 chuck.

11
12 52. The apparatus of claim 51 wherein the substrate comprises
13 a bulk semiconductor wafer.

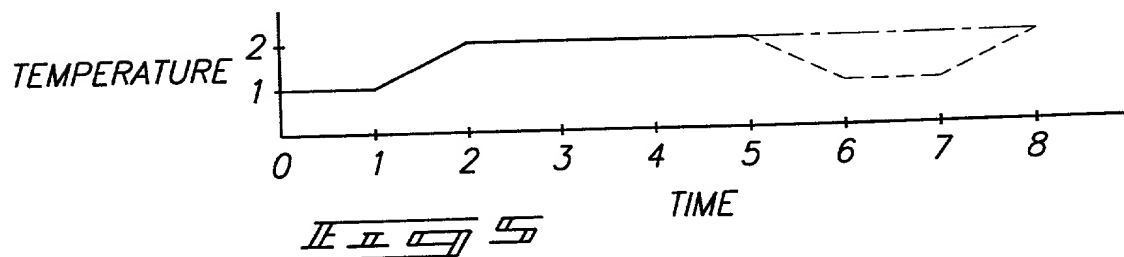
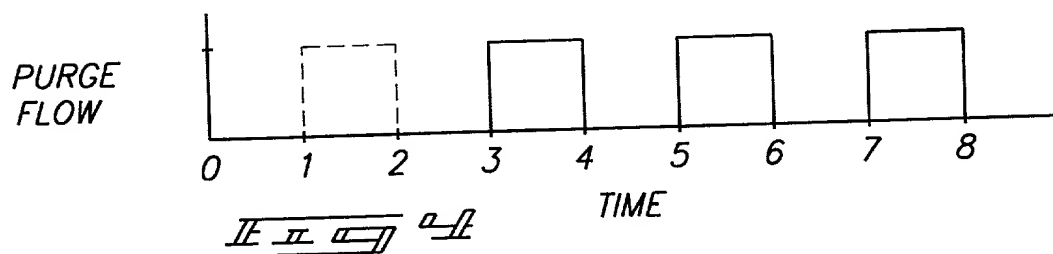
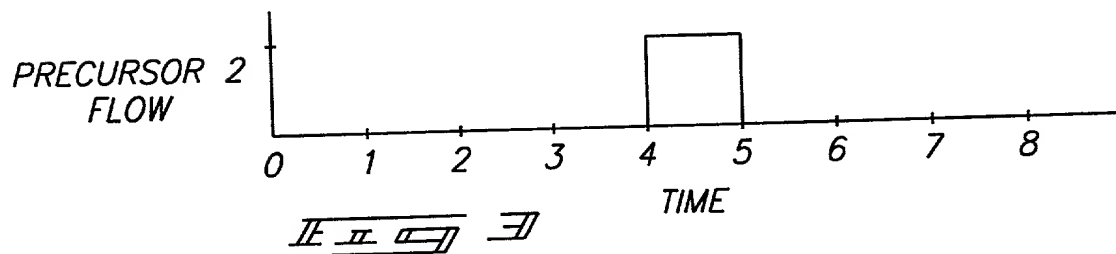
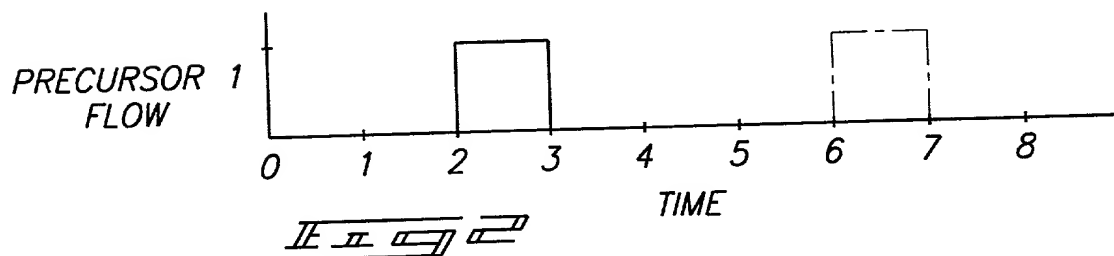
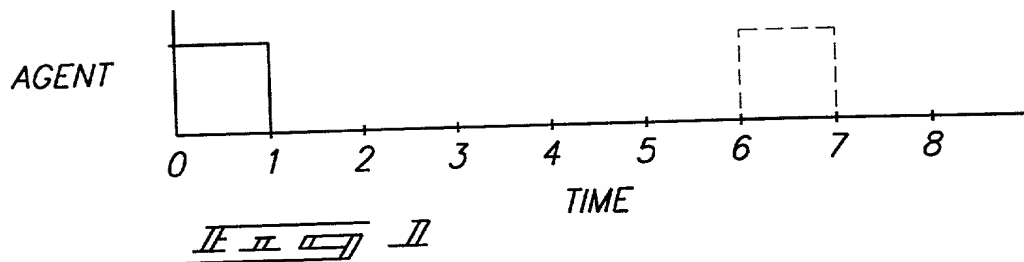
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15 53. The apparatus of claim 51 wherein the substrate lift lowers
16 a deposition substrate from the elevation above the heated surface of the
17 substrate chuck when dispensing precursor gas in the at least one
18 contacting chamber.

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20 54. The apparatus of claim 51 wherein the substrate lift
21 comprises positioning pins of the heated substrate chuck.

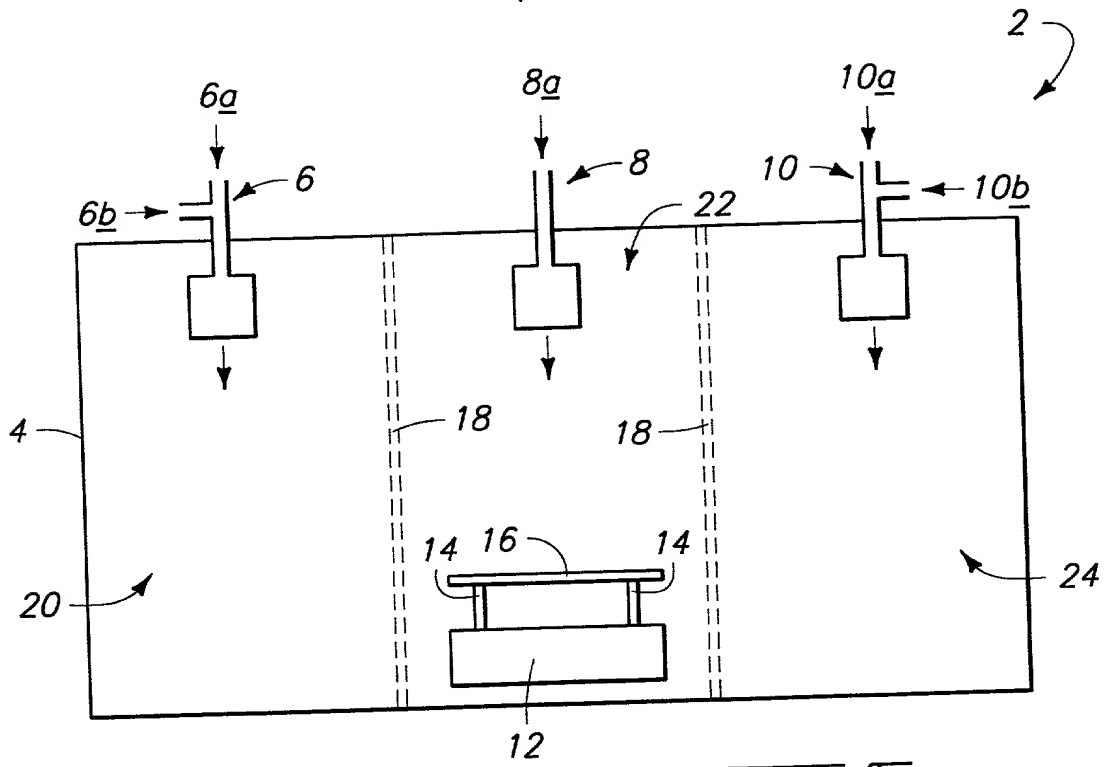
ABSTRACT OF THE DISCLOSURE

A deposition method includes, at a first temperature, contacting a substrate with a surface activation agent and adsorbing a first layer over the substrate. At a second temperature greater than the first temperature, the first layer may be contacted with a first precursor, chemisorbing a second layer at least one monolayer thick over the substrate. The first layer may enhance a chemisorption rate of the first precursor compared to the substrate without the surface activation agent adsorbed thereon. One deposition apparatus includes a deposition chamber with a precursor gas dispenser in a contacting zone and a cooling gas dispenser in a cooling zone. A substrate chuck moves by linear translational motion from the contacting zone to the cooling zone. The substrate chuck includes a substrate lift that positions a deposition substrate at an elevation above a heated surface of the substrate chuck when dispensing a cooling gas or surface activation agent. Another deposition apparatus includes a cooling chamber with a cooled substrate chuck and a contacting chamber with a heated substrate chuck. The contacting chamber also has a precursor gas dispenser and the heated substrate chuck includes a substrate lift. A robotic substrate handler moves a substrate from the cooled substrate chuck to the heated substrate chuck.

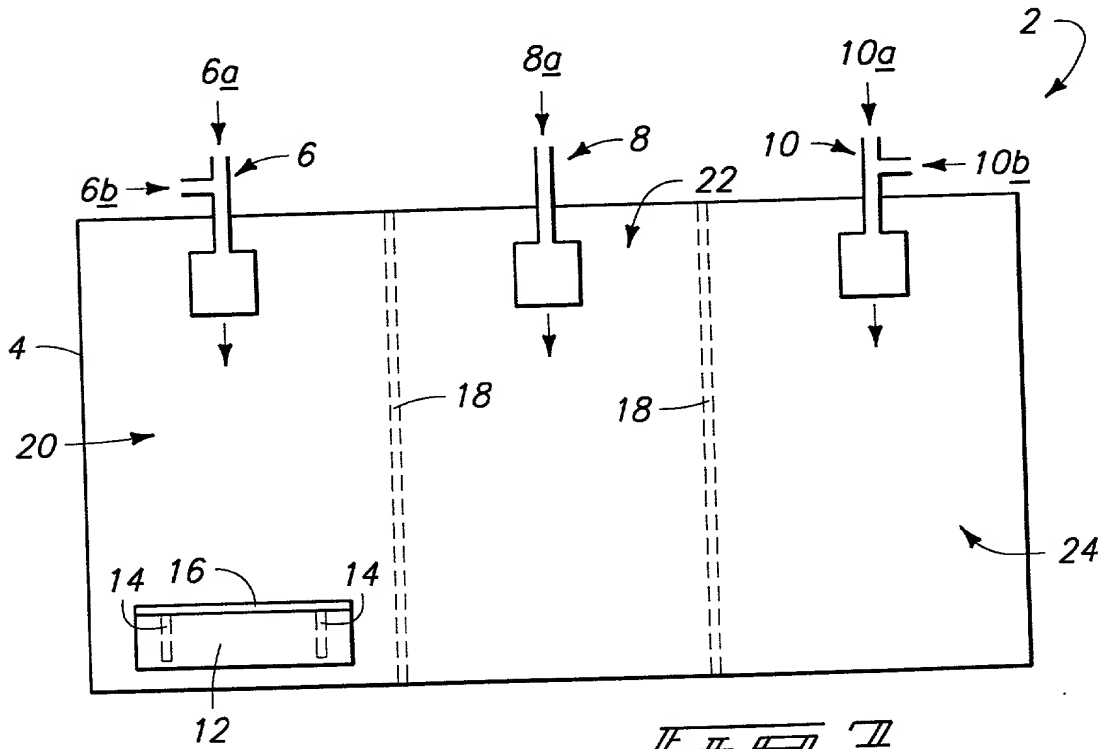
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